



## Impact of graphene on ZnO assisted photocatalysis for degradation of lignin rich substrates by UV/Iodide process

Mazarji, M.; Alvarado-Morales, Merlin; Tsapekos, Panagiotis; Nabi-Bidhendi, G.; Mahmoodi, N. M.; Angelidaki, Irini

*Publication date:*  
2018

*Document Version*  
Peer reviewed version

[Link back to DTU Orbit](#)

*Citation (APA):*  
Mazarji, M., Alvarado-Morales, M., Tsapekos, P., Nabi-Bidhendi, G., Mahmoodi, N. M., & Angelidaki, I. (2018). *Impact of graphene on ZnO assisted photocatalysis for degradation of lignin rich substrates by UV/Iodide process*. Abstract from Biogas Science 2018, Torino, Italy.

---

### General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

# IMPACT OF GRAPHENE ON ZNO ASSISTED PHOTOCATALYSIS FOR DEGRADATION OF LIGNIN RICH SUBSTRATES BY UV/IODIDE PROCESS

Mazarji, M.<sup>1,2</sup>, Alvarado-Morales, M.<sup>2</sup>, Tsapekos, P.<sup>2</sup>, Nabi-Bidhendi, G.<sup>1</sup>, Mahmoodi, NM.<sup>3</sup>,  
Angelidaki, I.<sup>2</sup>

<sup>1</sup>*Department of Environmental Engineering, Graduate Faculty of Environment, University of Tehran, 1417853111, Tehran, Iran*

<sup>2</sup>*Technical University of Denmark, Department of Environmental Engineering, Building 113, DK-2800 Kgs. Lyngby, Denmark*

<sup>3</sup>*Department of Environmental Research, Institute for Color Science and Technology, 16765-654, Tehran, Iran*

e-mail of the corresponding author: iria@env.dtu.dk

**Keywords:** UV/Iodide; Lignin Valorisation; Graphene; Phenolic Preservation.

## INTRODUCTION

Despite many efforts have been done to develop efficient lignin oxidative depolymerization strategies, there is still remaining issue of uncontrollable overoxidation to gaseous products (Sun et al. 2018). Several research groups are investigating different pretreatment methods to target cleaving abundance of  $\beta$ -O-4 linkages (less recalcitrant with bond strength estimation of 290~305 kJ/mol) or the 5-5' biphenyl type linkages (more recalcitrant with bond strength estimation of 490 kJ/mol) to produce different compounds. Due to this high thermal and chemical stability of C-C and C-O bonds, lignin is resistant to physical, chemical and biological degradation (Pineda and Lee 2016). Iodide photolysis (UV/Iodide) under UV illumination affords an effective method to produce hydrated electrons ( $e_{aq}^-$ ) and iodine radical ( $I^\bullet$ ), which in turn could degrade many recalcitrant pollutants (Sun et al. 2017). UV/Iodide can be further enhanced by the addition of zinc oxide (ZnO) photocatalyst. In the presence of ZnO, iodide can act as a sacrificial electron donor (ED). In this system, the primary role of ED is to form a charge transfer (CT) complex between semiconductor and ED in order to react irreversibly with the photo-generated valence bond holes in ZnO. The enhanced photocatalytic electron/hole separation could result in higher overall quantum efficiency. On the other hand, the presence of  $I^\bullet$  appears as a factor for decreased selectivity. Thus, a selective product formation while maintaining high conversion values remains a challenge. Addition of Graphene (Gr) in UV/Iodide/ZnO system could trap  $e_{aq}^-$  due to the extraordinary potential of nanosheets, pawing their route to the conduction band of the semiconductor. As a result, by forcing electron injection from Gr into its n-type counterpart (i.e. ZnO), and Gr in turn receives and transports holes for subsequent iodide oxidation instead of water. In the present study, a novel approach is developed for hindering the production of  $^\bullet\text{OH}$  radical which is responsible for degradation of valuable chemicals (i.e. phenolics). The approach was applied as a mean to increase the bioavailability of wheat straw for enhanced biogas production. Production and perservation from overoxidation of phenolics without compromising lignin degradation yield was explored.

## MATERIALS AND METHODS

The modified Hummers' method was followed for synthesizing graphite oxide nanoparticles (Hosseinabadi-Farahani et al. 2014). The synthesis of ZnO incorporated with 1.2 mg/mL Gr was conducted based on Mazarji et al. (2017). A UV doped medium pressure lamp (SR HUV700, 700 W) was used for the photocatalytic experiments. The concentration of total phenolic compound (TPC) was determined according to the Folin-Ciocalteu method (Ainsworth and Gillespie 2007). The influence of the photocatalysis on biomass biodegradability was assessed using batch tests (Angelidaki et al. 2009).

## RESULTS AND DISCUSSION

As can be seen in Fig. 1a, Abs<sub>280</sub> decreased over photocatalysis time. This trend was more pronounced in case of lignin soaked into alkaline medium, compared to straw. TPC also showed the sharp decrease in the first hour of irradiation, however there was no significant change occurred beyond the first hour. This might be due to the possible interaction between the  $\pi$  system of graphene and the  $\pi$  unit of phenolics which in turn hindered the adsorbed of valuable phenolic. As shown for straw soaked into water, there was no significant change for both Abs and TPC during photocatalysis. The reason for poor photocatalysis might be attributed to the fact that the alkaline condition is necessary for forming CT mechanism. Due to the increased efficiency at alkaline condition, a set of biodegradability experiments was carried out for straw and lignin soaked with NaOH to examine the potential of using the photocatalytically pretreated biomass and lignin for biogas production. For both treated samples, higher methane production was observed compared to their corresponding untreated samples (Fig. 1b). The results from monitoring the methane production showed that lignin was disrupted and bioavailable material was served for enhanced produced that in turn favored methane yield.

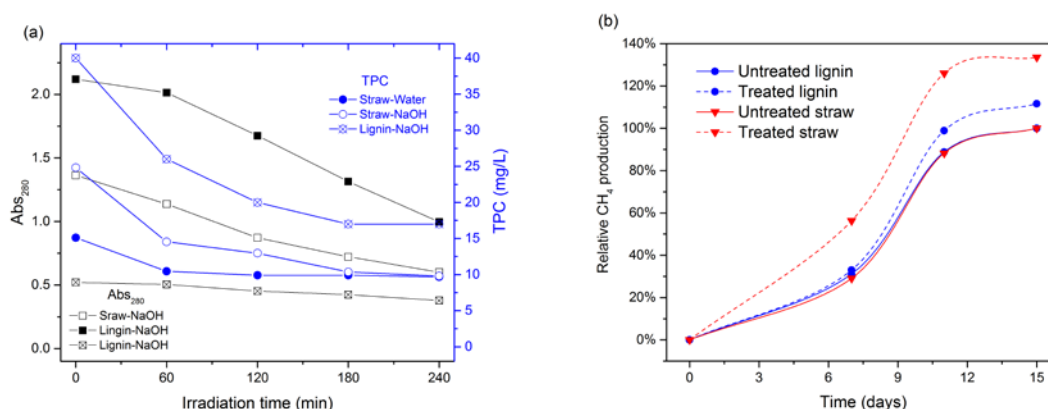


Fig. 1: Lignin and TPC degradation in UV/KI/ZnO-G1.2 system; (photocatalyst dosage 50 mg/L, Lignin con. 100 mg/L, WS con. 1 g/L, NaOH 25 mM, KI 1 mM) (a) and methane yields of untreated lignin and degraded lignin (b)

## CONCLUSION

Novel solution method for selective lignin depolymerisation strategy using graphene (Gr) was developed. UV/Iodide/ZnO-Gr process exhibited selective photocatalytic activity for lignin degradation due to the condition provided by the presence of Gr. In this system,  $e_{aq}^-$  easily flows into ZnO through Gr. In exchange, Gr receives photogenerated holes with less oxidative power. As a result, the production of  $\bullet\text{OH}$  which is responsible for degradation of phenolics becomes restricted. The photocatalytic treatment of lignin and straw had positive effect on methane production.

## REFERENCES

- Ainsworth EA, Gillespie KM. 2007. Nature protocols 2, 875–877.
- Angelidaki I, Alves M, Bolzonella D, Borzacconi L, Campos JL, Guwy AJ, Kalyuzhnyi S, Jenicek P, Van Lier JB. 2009. Water Science and Technology 59, 927–934.
- Hosseiniabadi-Farahani Z, Hosseini-Monfared H, Mahmoodi NM. 2014. Desalination and Water Treatment, 1–13.
- Mazarji M, Nabi-Bidhendi G, Mahmoodi NM. 2017. Journal of the Taiwan Institute of Chemical Engineers.
- Pineda A, Lee AF. 2016. Applied Petrochemical Research 6, 243–256.
- Sun Z, Fridrich B, de Santi A, Elangovan S, Barta K. 2018. Chemical reviews.
- Sun Z, Zhang C, Chen P, Zhou Q, Hoffmann MR. 2017. Water research 127, 50–58.